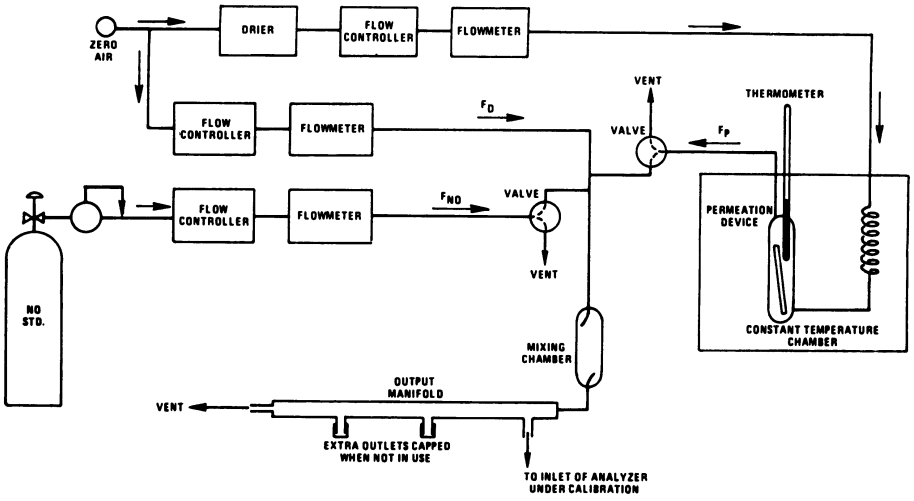

Figure 2. Schematic diagram of a typical calibration apparatus using an NO_2 permeation device.

[41 FR 52688, Dec. 1, 1976, as amended at 48 FR 2529, Jan. 20, 1983]

Appendix G to Part 50—Reference Method for the Determination of Lead in Total Suspended Particulate Matter

1.0 Scope and Applicability

Based on review of the air quality criteria and national ambient air quality standard (NAAQS) for lead (Pb) completed in 2008, the EPA made revisions to the primary and secondary NAAQS for Pb to protect public health and welfare. The EPA revised the level from 1.5 $\mu g/m^3$ to 0.15 $\mu g/m^3$ while retaining the current indicator of Pb in total suspended particulate matter (Pb-TSP).

Pb-TSP is collected for 24 hours on a TSP filter as described in Appendix B of part 50, the Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). This method is for the analysis of Pb from TSP filters by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) using a heated ultrasonic bath with nitric acid (HNO_3) and hydrochloric acid (HCl) or a heated block (hot block) digester with HNO_3 for filter extraction.

This method is based on the EPA's Office of Solid Waste (SW–846) Method 6020A—Inductively Coupled Plasma Mass Spectrometry (U.S. EPA, 2007). Wording in certain sections of this method is paraphrased or taken directly from Method 6020A.

1.1 ICP–MS is applicable for the sub-µg/mL (ppb) determination of Pb in a wide variety of matrices. Results reported for monitoring or compliance purposes are calculated in $\mu g/m^3$ at local conditions (LC). This procedure describes a method for the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or PTFE filters and measurement of the extracted Pb using ICP–MS.

1.2 Due to variations in the isotopic abundance of Pb, the value for total Pb must be based on the sum of the signal intensities for isotopic masses, 206, 207, and 208. Most instrument software packages are able to sum the primary isotope signal intensities automatically.

1.3 ICP–MS requires the use of an internal standard. ^{115}In (Indium), ^{165}Ho (Holmium), and ^{209}Bi (Bismuth) are recommended internal standards for the determination of Pb.

1.4 Use of this method is restricted to use by, or under supervision of, properly trained and experienced laboratory personnel. Requirements include training and experience in inorganic sample preparation, including acid extraction, and also knowledge in the recognition and in the correction of spectral, chemical and physical interference in ICP–MS.

2.0 Summary of Method

2.1 This method describes the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or PTFE ambient air filters with subsequent measurement of Pb by

ICP–MS. Estimates of the Method Detection Limit (MDL) or sensitivity of the method are provided in Tables 1, 3 and 5 and determined using Pb-spiked filters or filter strips analyzed in accordance with the guidance provided in 40 CFR 136, Appendix B—Determination and procedures for the Determination of the Method Detection Limit—Revision 1.1. The analytical range of the method is 0.00024 $\mu g/m^3$ to 0.60 $\mu g/m^3$, and based on the low and high calibration curve standards and a nominal filter sample volume of 2000 m^3.

2.2 This method includes two extraction methods. In the first method, a solution of HNO_3 and HCl is added to the filters or filter strips in plastic digestion tubes and the tubes are placed in a heated ultrasonic bath for one hour to facilitate the extraction of Pb. Following ultrasonication, the samples are brought to a final volume of 40 mL (50 mL for PTFE filters), vortex mixed or shaken vigorously, and centrifuged prior to aliquots being taken for ICP–MS analysis. In the second method, a solution of dilute HNO_3 is added to the filter strips in plastic digestion tubes and the tubes placed into the hot block digester. The filter strip is completely covered by the solution. The tubes are covered with polypropylene watch glasses and refluxed. After reflux, the samples are diluted to a final volume of 50 mL with reagent water and mixed before analysis.

2.3 Calibration standards and check standards are prepared to matrix match the acid composition of the samples. ICP–MS analysis is then performed. With this method, the samples are first aspirated and the aerosol thus created is transported by a flow of argon gas into the plasma torch. The ions produced (*e.g.*, Pb^{+1}) in the plasma are extracted via a differentially-pumped vacuum interface and are separated on the basis of their mass-to-charge ratio. The ions are quantified by a channel electron multiplier or a Faraday detector and the signal collected is processed by the instrument's software. Interferences must be assessed and corrected for, if present.

3.0 Definitions

Pb—Elemental or ionic lead
HNO_3—Nitric acid
HCl—Hydrochloric acid
ICP–MS—Inductively Coupled Plasma Mass Spectrometer
MDL—Method detection limit
RSD—Relative standard deviation
RPD—Relative percent difference
CB—Calibration Blank
CAL—Calibration Standard
ICB—Initial calibration blank
CCB—Continuing calibration blank
ICV—Initial calibration verification
CCV—Continuing calibration verification
LLCV—Lower Level Calibration Verification, serves as the lower level ICV and lower level CCV
RB—Reagent blank
RBS—Reagent blank spike
MSDS—Material Safety Data Sheet
NIST—National Institute of Standards and Technology
D.I. water—Deionized water
SRM—NIST Standard Reference Material
CRM—Certified Reference Material
EPA—Environmental Protection Agency
v/v—Volume to volume ratio

4.0 Interferences

4.1 Reagents, glassware, plasticware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. If reagent blanks, filter blanks, or quality control blanks yield results above the detection limit, the source of contamination must be identified. All containers and reagents used in the processing of the samples must be checked for contamination prior to sample extraction and analysis. Reagents shall be diluted to match the final concentration of the extracts and analyzed for Pb. Labware shall be rinsed with dilute acid solution and the solution analyzed. Once a reagent or labware article (such as extraction tubes) from a manufacturer has been successfully screened, additional screening is not required unless contamination is suspected.

4.2 Isobaric elemental interferences in ICP–MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the species of interest. There are no species found in ambient air that will result in isobaric interference with the three Pb isotopes (206, 207, and 208) being measured. Polyatomic interferences occur when two or more elements combine to form an ion with the same mass-to-charge ratio as the isotope being measured. Pb is not subject to interference from common polyatomic ions and no correction is required.

4.3 The distribution of Pb isotopes is not constant. The analysis of total Pb should be based on the summation of signal intensities for the isotopic masses 206, 207, and 208. In most cases, the instrument software can perform the summation automatically.

4.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers of the ICP–MS. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. These interferences are compensated for by use of internal standards. Sample dilution will reduce the effects of high levels of dissolved salts, but calibration standards

must be prepared in the extraction medium and diluted accordingly.

4.5 Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

5.0 Health and Safety Cautions

5.1 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in the chemical analysis. Specifically, concentrated HNO_3 presents various hazards and is moderately toxic and extremely irritating to skin and mucus membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 Concentrated HNO_3 and HCl are moderately toxic and extremely irritating to the skin. Use these reagents in a fume hood, and if eye and skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. The component of this procedure requiring the greatest care is HNO_3. HNO_3 is a strong, corrosive, oxidizing agent that requires protection of the eyes, skin, and clothing. Items to be worn during use of this reagent include:

1. Safety goggles (or safety glasses with side shields),
2. Acid resistant rubber gloves, and
3. A protective garment such as a laboratory apron. HNO_3 spilled on clothing will destroy the fabric; contact with the skin underneath will result in a burn.

It is also essential that an eye wash fountain or eye wash bottle be available during performance of this method. An eye wash bottle has a spout that covers the eye. If acid or any other corrosive gets into the eye, the water in this bottle is squirted onto the eye to wash out the harmful material. Eye washing should be performed with large amounts of water immediately after exposure. Medical help should be sought immediately after washing. If either acid, but especially HNO_3, is spilled onto the skin, wash immediately with large amounts of water. Medical attention is not required unless the burn appears to be significant. Even after washing and drying, HNO_3 may leave the skin slightly brown in color; this will heal and fade with time.

5.3 Pb salts and Pb solutions are toxic. Great care must be taken to ensure that samples and standards are handled properly; wash hands thoroughly after handling.

5.4 Care must be taken when using the ultrasonic bath and hot block digester as they are capable of causing mild burns. Users should refer to the safety guidance provided by the manufacturer of their specific equipment.

5.5 Analytical plasma sources emit radio frequency radiation in addition to intense ultra violet (UV) radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

6.0 Equipment

6.1 Thermo Scientific X-Series ICP–MS or equivalent. The system must be capable of providing resolution better or equal to 1.0 atomic mass unit (amu) at 10 percent peak height. The system must have a mass range from at least 7 to 240 amu that allows for the application of the internal standard technique. For the measurement of Pb, an instrument with a collision or reaction cell is not required.

6.2 Ultrasonic Extraction Equipment

6.2.1 Heated ultrasonic bath capable of maintaining a temperature of 80 °C; VWR Model 750HT, 240W, or equivalent. Ultrasonic bath must meet the following performance criteria:

1. Cut a strip of aluminum foil almost the width of the tank and double the depth.
2. Turn the ultrasonic bath on and lower the foil into the bath vertically until almost touching the bottom of the tank and hold for 10 seconds.
3. Remove the foil from the tank and observe the distribution of perforations and small pin prick holes. The indentations should be fine and evenly distributed. The even distribution of indentations indicates the ultrasonic bath is acceptable for use.

6.2.2 Laboratory centrifuge, Beckman GS–6, or equivalent.

6.2.3 Vortex mixer, VWR Signature Digital Vortex Mixer, VWR Catalog No. 14005–824, or equivalent.

6.3 Hot block extraction equipment

6.3.1 Hot block digester, SCP Science DigiPrep Model MS, No. 010–500–205 block digester capable of maintaining a temperature of 95 °C, or equivalent.

6.4 Materials and Supplies

• Argon gas supply, 99.99 percent purity or better. National Welders Microbulk, or equivalent.

• Plastic digestion tubes with threaded caps for extraction and storage, SCP Science DigiTUBE® Item No. 010–500–063, or equivalent.

• Disposable polypropylene ribbed watch glasses (for heated block extraction), SCP Science Item No. 010–500–081, or equivalent.

• Pipette, Rainin EDP2, 100 µL, ±1 percent accuracy, ≤1 percent RSD (precision), with disposable tips, or equivalent.

• Pipette, Rainin EDP2, 1000 µL, ±1 percent accuracy, ≤1 percent RSD (precision), with disposable tips, or equivalent.

• Pipette, Rainin EDP2, 1–10 mL, ±1 percent accuracy, ≤1 percent RSD (precision), with disposable tips, or equivalent.

• Pipette, Thermo Lab Systems, 5 mL, ±1 percent accuracy, ≤1 percent RSD (precision), with disposable tips, or equivalent.

• Plastic tweezer, VWR Catalog No. 89026–420, or equivalent.

• Laboratory marker.

• Ceramic knife, Kyocera LK–25, and nonmetal ruler or other suitable cutting tools for making straight cuts for accurately measured strips.

• Blank labels or labeling tape, VWR Catalog No. 36425–045, or equivalent.

• Graduated cylinder, 1 L, VWR 89000–260, or equivalent.

• Volumetric flask, Class A, 1 L, VWR Catalog No. 89025–778, or equivalent.

• Millipore Element deionized water system, or equivalent, capable of generating water with a resistivity of ≥17.9 MΩ-cm).

• Disposable syringes, 10-mL, with 0.45 micron filters (must be Pb-free).

• Plastic or PTFE wash bottles.

• Glassware, Class A—volumetric flasks, pipettes, and graduated cylinders.

• Glass fiber, quartz, or PTFE filters from the same filter manufacturer and lot used for sample collection for use in the determination of the MDL and for laboratory blanks.

7.0 Reagents and Standards

7.1 Reagent—or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.2 Concentrated nitric acid, 67–70 percent, SCP Science Catalog No. 250–037–177, or equivalent.

7.3 Concentrated hydrochloric acid (for the ultrasonic extraction method), 33–36 percent, SCP Science Catalog No. 250–037–175, or equivalent.

7.4 Deionized water—All references to deionized water in the method refer to deionized water with a resistivity ≥17.9 MΩ-cm.

7.5 Standard stock solutions may be commercially purchased for each element or as a multi-element mix. Internal standards may be purchased as a mixed multi-element solution. The manufacturer's expiration date and storage conditions must be adhered to.

7.5.1 Lead standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100028–1, or equivalent.

7.5.2 Indium (In) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100024–1, or equivalent.

7.5.3 Bismuth (Bi) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100006–1, or equivalent.

7.5.4 Holmium (Ho) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100023–1, or equivalent.

7.5.5 Second source lead standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. Must be from a different vendor or lot than the standard described in 7.5.1. Inorganic Ventures Catalog No. CGPB–1, or equivalent.

7.5.6 Standard Reference Materials, NIST SRM 2583, 2586, 2587 or 1648, or equivalent.[5]

Note: The In, Bi, and Ho internal standards may also be purchased as 10 µg/mL standards. Calibration standards are prepared by diluting stock standards to the appropriate levels in the same acid concentrations as in the final sample volume. The typical range for calibration standards is 0.001 to 2.00 µg/mL. At a minimum, the curve must contain a blank and five Pb containing calibration standards. The calibration standards are stored at ambient laboratory temperature. Calibration standards must be prepared weekly and verified against a freshly prepared ICV using a NIST-traceable source different from the calibration standards.

7.6 Internal standards may be added to the test solution or by on-line addition. The nominal concentration for an internal standard is 0.010 µg/mL (10 ppb). Bismuth (Bi) or holmium (Ho) are the preferred internal standards for Pb, but indium (In) may be used in the event the sample contains Bi and high recoveries are observed.

7.7 Three laboratory blank solutions are required for analysis: (1) The calibration

[5] Certificates of Analysis for these SRMs can be found at: *http://www.nist.gov/srm/index.cfm*.

blank is used in the construction of the calibration curve and as a periodic check of system cleanliness (ICB and CCB); (2) the reagent blank (RB) is carried through the extraction process to assess possible contamination; and (3) the rinse blank is run between samples to clean the sample introduction system. If RBs or laboratory blanks yield results above the detection limit, the source of contamination must be identified. Screening of labware and reagents is addressed in Section 4.1.

7.7.1 The calibration blank is prepared in the same acid matrix as the calibration standards and samples and contains all internal standards used in the analysis.

7.7.2 The RB contains all reagents used in the extraction and is carried through the extraction procedure at the same time as the samples.

7.7.3 The rinse blank is a solution of 1 to 2 percent HNO_3 (v/v) in reagent grade water. A sufficient volume should be prepared to flush the system between all standards and samples analyzed.

7.7.4 The EPA currently provides glass fiber, quartz, and PTFE filters to air monitoring agencies as requested annually. As part of the procurement process, these filters are tested for acceptance by the EPA. The current acceptance criteria for glass fiber and quartz filters is 15 µg per filter or 0.0075 $\mu g/m^3$ using a nominal sample volume of 2000 m^3 and 4.8 ng/cm^2 or 0.0024 $\mu g/m^3$ for PTFE filters using a nominal sample volume of 24 m^3. Acceptance test results for filters obtained by the EPA are typically well below the criterion specified and also below the recently revised Pb method performance detection limit of 0.0075 $\mu g/m^3$; therefore, blank subtraction should not be performed.

7.7.5 If filters are not provided by the EPA for sample collection and analysis, filter lot blanks should be analyzed for Pb content. For large filter lots (≤500 filters), randomly select 20 to 30 filters from the lot and analyze the filter or filter strips for Pb. For smaller filter lots, a lesser number of filters can be analyzed. Glass, quartz and PTFE filters must not have levels of Pb above the criteria specified in section 7.7.4 and, therefore, blank correction should not be performed. If acceptance testing shows levels of Pb above the criteria in Section 7.7.4, corrective action must be taken to reduce the levels before proceeding.

7.8 The Initial Calibration Verification (ICV), Lower Level Calibration Verification (LLCV), and Continuing Calibration Verification (CCV) solutions are prepared from a different Pb source than the calibration curve standards and at a concentration that is either at or below the midpoint on the calibration curve, but within the calibration range. Both are prepared in the same acid matrix as the calibration standards. Note that the same solution may be used for both the ICV and CCV. The ICV/CCV and LLCV solutions must be prepared fresh daily.

7.9 Tuning Solution. Prepare a tuning solution according to the instrument manufacturer's recommendations. This solution will be used to verify the mass calibration and resolution of the instrument.

8.0 Quality Control (QC)

8.1 Standard QC practices shall be employed to assess the validity of the data generated, including: MDL, RB, duplicate samples, spiked samples, serial dilutions, ICV, CCV, LLCV, ICB, CCB, and SRMs/CRMs.

8.2 MDLs must be calculated in accordance with 40 CFR part 136, Appendix B. RBs with low-level standard spikes are used to estimate the MDL. The low-level standard spike is added to at least 7 individual filter strips and then carried through the entire extraction procedure. This will result in at least 7 individual samples to be used for the MDL. The recommended range for spiking the strips is 1 to 5 times the estimated MDL.

8.3 For each batch of samples, one RB and one reagent blank spike (RBS) that is spiked at the same level as the sample spike (see Section 8.6) must be prepared and carried throughout the entire process. The results of the RB must be below 0.001 µg/mL. The recovery for the RBS must be within ±20 percent of the expected value. If the RB yields a result above 0.001 µg/mL, the source of contamination must be identified and the extraction and analysis repeated. Reagents and labware must be suspected as sources of contamination. Screening of reagents and labware is addressed in Section 4.1.

8.4 Any samples that exceed the highest calibration standard must be diluted and rerun so that the concentration falls within the curve. The minimum dilution will be 1 to 5 with matrix matched acid solution.

8.5 The internal standard response must be monitored during the analysis. If the internal standard response falls below 70 percent or rises above 120 percent of expected due to possible matrix effects, the sample must be diluted and reanalyzed. The minimum dilution will be 1 to 5 with matrix matched acid solution. If the first dilution does not correct the problem, additional dilutions must be run until the internal standard falls within the specified range.

8.6 For every batch of samples prepared, there must be one duplicate and one spike sample prepared. The spike added is to be at a level that falls within the calibration curve, normally the midpoint of the curve. The initial plus duplicate sample must yield a relative percent difference ≤20 percent. The spike must be within ±20 percent of the expected value.

8.7 For each batch of samples, one extract must be diluted five-fold and analyzed. The corrected dilution result must be within ±10

percent of the undiluted result. The sample chosen for the serial dilution shall have a concentration at or above 10X the lowest standard in the curve to ensure the diluted value falls within the curve. If the serial dilution fails, chemical or physical interference should be suspected.

8.8 ICB, ICV, LLCV, CCB and CCV samples are to be run as shown in the following table.

Sample	Frequency	Performance specification
ICB	Prior to first sample	Less than 0.001 μg/mL.
ICV	Prior to first sample	Within 90 to 110 percent of the expected value.
LLCV	Daily, before first sample and after last sample	±10 percent of the expected value.
CCB	After every 10 extracted samples	Less than 0.001 μg/mL.
CCV	After every 10 extracted samples	Within 90–110 percent of the expected value.

If any of these QC samples fails to meet specifications, the source of the unacceptable performance must be determined, the problem corrected, and any samples not bracketed by passing QC samples must be reanalyzed.

8.9 For each batch of samples, one certified reference material (CRM) must be combined with a blank filter strip and carried through the entire extraction procedure. The result must be within ±10 percent of the expected value.

8.10 For each run, a LLCV must be analyzed. The LLCV must be prepared at a concentration not more than three times the lowest calibration standard and at a concentration not used in the calibration curve. The LLCV is used to assess performance at the low end of the curve. If the LLCV fails (±10 percent of the expected value) the run must be terminated, the problem corrected, the instrument recalibrated, and the analysis repeated.

8.11 Pipettes used for volumetric transfer must have the calibration checked at least once every 6 months and pass ±1 percent accuracy and ≤1 percent RSD (precision) based on five replicate readings. The pipettes must be checked weekly for accuracy with a single replicate. Any pipette that does not meet ±1 percent accuracy on the weekly check must be removed from service, repaired, and pass a full calibration check before use.

8.12 Samples with physical deformities are not quantitatively analyzable. The analyst should visually check filters prior to proceeding with preparation for holes, tears, or non-uniform deposit which would prevent representative sampling. Document any deformities and qualify the data with flags appropriately. Care must be taken to protect filters from contamination. Filters must be kept covered prior to sample preparation.

9.0 ICP MS Calibration

Follow the instrument manufacturer's instructions for the routine maintenance, cleaning, and ignition procedures for the specific ICP–MS instrument being used.

9.1 Ignite the plasma and wait for at least one half hour for the instrument to warm up before beginning any pre-analysis steps.

9.2 For the Thermo X-Series with Xt cones, aspirate a 10 ng/mL tuning solution containing In, Bi, and Ce (Cerium). Monitor the intensities of In, Bi, Ce, and CeO (Cerium oxide) and adjust the instrument settings to achieve the highest In and Bi counts while minimizing the CeO/Ce oxide ratio. For other instruments, follow the manufacturer's recommended practice. Tune to meet the instrument manufacturer's specifications. After tuning, place the sample aspiration probe into a 2 percent HNO_3 rinse solution for at least 5 minutes to flush the system.

9.3 Aspirate a 5 ng/mL solution containing Co, In, and Bi to perform a daily instrument stability check. Run 10 replicates of the solution. The percent RSD for the replicates must be less than 3 percent at all masses. If the percent RSD is greater than 3 percent, the sample introduction system, pump tubing, and tune should be examined, and the analysis repeated. Place the sample aspiration probe into a 2 percent HNO_3 rinse solution for at least 5 minutes to flush the system.

9.4 Load the calibration standards in the autosampler and analyze using the same method parameters that will be used to analyze samples. The curve must include one blank and at least 5 Pb-containing calibration standards. The correlation coefficient must be at least 0.998 for the curve to be accepted. The lowest standard must recover ±15 percent of the expected value and the remaining standards must recover ±10 percent of the expected value to be accepted.

9.5 Immediately after the calibration curve is completed, analyze an ICV and an ICB. The ICV must be prepared from a different source of Pb than the calibration standards. The ICV must recover 90–110 percent of the expected value for the run to continue. The ICB must be less than 0.001 μg/mL. If either the ICV or the ICB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started.

9.6 A LLCV, CCV and a CCB must be run after the ICV and ICB. A CCV and CCB must be run at a frequency of not less than every 10 extracted samples. A typical analytical run sequence would be: Calibration blank, Calibration standards, ICV, ICB, LLCV, CCV,

CCB, Extracts 1–10, CCV, CCB, Extracts 11–20, CCV, CCB, Extracts 21–30, CCV, CCB, LLCV, CCV, CCB. Extracts are any field sample or QC samples that have been carried through the extraction process. The CCV solution is prepared from a different source than the calibration standards and may be the same as the ICV solution. The LLCV must be within ±10 percent of expected value. The CCV value must be within ±10 percent of expected for the run to continue. The CCB must be less than 0.001 µg/mL. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

9.7 A LLCV, CCV, and CCB set must be run at the end of the analysis. The LLCV must be within ±30 percent of expected value. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

10.0 Heated Ultrasonic Filter Strip Extraction

All plasticware (*e.g.,* Nalgene) and glassware used in the extraction procedures is soaked in 1 percent HNO_3 (v/v) for at least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to ±1 percent accuracy and ≤1 percent RSD at a minimum of once every 6 months.

10.1 Sample Preparation—Heated Ultrasonic Bath

10.1.1 Extraction solution (1.03M HNO_3 + 2.23M HCl). Prepare by adding 500 mL of deionized water to a 1000 mL flask, adding 64.4 mL of concentrated HNO_3 and 182 mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

10.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb. Cut a ¾ inch X 8 inch strip from the glass fiber or quartz filter by cutting a strip from the edge of the filter where it has been folded along the 10 inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging deposits.

10.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled strip in the bottom of a labeled 50 mL extraction tube. In a fume hood, add 15.00 ±0.15 mL of the extraction solution (see Section 10.1.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

10.1.4 Loosely cap the 50 mL extraction tube and place it upright in a plastic rack. When all samples have been prepared, place the racks in an uncovered heated ultrasonic water bath that has been preheated to 80 ±5 °C and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour ±5 minutes at 80 ±5 °C.

10.1.5 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.

10.1.6 Add 25.00 ±0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 40.0 ±0.4 mL. Tightly cap the tubes, and vortex mix or shake vigorously. Place the extraction tubes in an appropriate holder and centrifuge for 20 minutes at 2500 revolutions per minute (RPM).

CAUTION—Make sure that the centrifuge holder has a flat bottom to support the flat bottomed extraction tubes.

10.1.7 Pour an aliquot of the solution into an autosampler vial for ICP–MS analysis to avoid the potential for contamination. Do not pipette an aliquot of solution into the autosampler vial.

10.1.8 Decant the extract to a clean tube, cap tightly, and store the sample extract at ambient laboratory temperature. Extracts may be stored for up to 6 months from the date of extraction.

10.2 47 mm PTFE Filter Extraction—Heated Ultrasonic Bath

10.2.1 Extraction solution (1.03M HNO_3 + 2.23M HCl). Prepare by adding 500 mL of D.I. water to a 1000mL flask, adding 64.4 mL of concentrated HNO_3 and 182 mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

10.2.2 Using plastic tweezers, bend the PTFE filter into a U-shape and insert the filter into a labeled 50 mL extraction tube with the particle loaded side facing the center of the tube. Gently push the filter to the bottom of the extraction tube. In a fume hood, add 25.00 ±0.15 mL of the extraction solution (see Section 10.2.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter.

10.2.3 Loosely cap the 50 mL extraction tube and place it upright in a plastic rack. When all samples have been prepared, place the racks in an uncovered heated ultrasonic water bath that has been preheated to 80 ±5 °C and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes, but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour ±5 minutes at 80 ±5 °C.

10.2.4 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.

10.2.5 Add 25.00 ±0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 50.0 ±0.4 mL. Tightly cap the tubes, and vortex mix or shake vigorously. Allow samples to stand for one hour to allow complete diffusion of the extracted Pb. The sample is now ready for analysis.

Note: Although PTFE filters have only been extracted using the ultrasonic extraction procedure in the development of this FRM, PTFE filters are inert and have very low Pb content. No issues are expected with the extraction of PTFE filters using the heated block digestion method. However, prior to using PTFE filters in the heated block extraction method, extraction method performance test using CRMs must be done to confirm performance (see Section 8.9).

11.0 Hot Block Filter Strip Extraction

All plasticware (*e.g.,* Nalgene) and glassware used in the extraction procedures is soaked in 1 percent HNO_3 for at least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to ±1 percent accuracy and ≤1 percent RSD at a minimum of once every 6 months.

11.1 Sample Preparation—Hot Block Digestion

11.1.1 Extraction solution (1:19, v/v HNO_3). Prepare by adding 500 mL of D.I. water to a 1000 mL flask, adding 50 mL of concentrated HNO_3, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. The extraction solution must be prepared at least weekly.

11.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb. Cut a 1-inch X 8-inch strip from the glass fiber or quartz filter. Cut a strip from the edge of the filter where it has been folded along the 10-inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging particle deposits.

11.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled strip in the bottom of a labeled 50 mL extraction tube. In a fume hood, add 20.0 ±0.15 mL of the extraction solution (see Section 11.1.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

11.1.4 Place the extraction tube in the heated block digester and cover with a disposable polyethylene ribbed watch glass. Heat at 95 ±5 °C for 1 hour and ensure that the sample does not evaporate to dryness. For proper heating, adjust the temperature control of the hot block such that an uncovered vessel containing 50 mL of water placed in the center of the hot block can be maintained at a temperature approximately, but no higher than 85C. Once the vessel is covered with a ribbed watch glass, the temperature of the water will increase to approximately 95 °C.

11.1.5 Remove the rack(s) from the heated block digester and allow the samples to cool.

11.1.6 Bring the samples to a final volume of 50 mL with D.I. water. Tightly cap the tubes, and vortex mix or shake vigorously for at least 5 seconds. Set aside (with the filter strip in the tube) for at least 30 minutes to allow the HNO_3 trapped in the filter to diffuse into the extraction solution.

11.1.7 Shake thoroughly (with the filter strip in the digestion tube) and let settle for at least one hour. The sample is now ready for analysis.

12.0 Measurement Procedure

12.1 Follow the instrument manufacturer's startup procedures for the ICP–MS.

12.2 Set instrument parameters to the appropriate operating conditions as presented in the instrument manufacturer's operating manual and allow the instrument to warm up for at least 30 minutes.

12.3 Calibrate the instrument per Section 9.0 of this method.

12.4 Verify the instrument is suitable for analysis as defined in Sections 9.2 and 9.3.

12.5 As directed in Section 8.0 of this method, analyze an ICV and ICB immediately after the calibration curve followed by a LLCV, then CCV and CCB. The acceptance requirements for these parameters are presented in Section 8.8.

12.6 Analyze a CCV and a CCB after every 10 extracted samples.

12.7 Analyze a LLCV, CCV and CCB at the end of the analysis.

12.8 A typical sample run will include field samples, field sample duplicates, spiked field sample extracts, serially diluted samples, the set of QC samples listed in Section 8.8 above, and one or more CRMs or SRMs.

12.9 Any samples that exceed the highest standard in the calibration curve must be diluted and reanalyzed so that the diluted concentration falls within the calibration curve.

13.0 Results

13.1 The filter results must be initially reported in µg/mL as analyzed. Any additional dilutions must be accounted for. The internal standard recoveries must be included in the result calculation; this is done by the ICP–MS software for most commercially-available instruments. Final results should be reported in µg Pb/m^3 to three significant figures as follows:

$C = ((\mu g\ Pb/mL * Vf * A)* D))/Vs$

Where:

C = Concentration, µg Pb/m^3
µg Pb/mL = Lead concentration in solution
Vf = Total extraction solution volume

A = Area correction; ¾″ × 8'' strip = 5.25 in^2 analyzed, A = 12.0 or 1'' × 8″ strip = 7 in^2 analyzed, A = 9.0
D = dilution factor (if required)
Vs = Actual volume of air sampled

The calculation assumes the use of a standard 8-inch × 10-inch TSP filter which has a sampled area of 9-inch × 7-inch (63.0 in^2) due to the ½-inch filter holder border around the outer edge. The ¾-inch × 8-inch strip has a sampled area of ¾-inch × 7-inch (5.25 in^2). The 1-inch × 8-inch strip has a sampled area of 1-inch × 7-inch (7.0 in^2). If filter lot blanks are provided for analysis, refer to Section 7.7.5 of this method for guidance on testing.

14.0 Method Performance

Information in this section is an example of typical performance results achieved by this method. Actual performance must be demonstrated by each individual laboratory and instrument.

14.1 Performance data have been collected to estimate MDLs for this method. MDLs were determined in accordance with 40 CFR 136, Appendix B. MDLs were estimated for glass fiber, quartz, and PTFE filters using seven reagent/filter blank solutions spiked with low level Pb at three times the estimated MDL of 0.001 μg/mL. Tables 1, 3, and 5 shows the MDLs estimated using both the ultrasonic and hot block extraction methods for glass fiber and quartz filters and the ultrasonic method for PTFE filters. The MDLs are well below the EPA requirement of five percent of the current Pb NAAQS or 0.0075 $\mu g/m^3$. These MDLs are provided to demonstrate the adequacy of the method's performance for Pb in TSP. Each laboratory using this method should determine MDLs in their laboratory and verify them annually. It is recommended that laboratories also perform the optional iterative procedure in 40 CFR 136, Appendix B to verify the reasonableness of the estimated MDL and subsequent MDL determinations.

14.2 Extraction method recovery tests with glass fiber and quartz filter strips, and PTFE filters spiked with NIST SRMs were performed using the ultrasonic/HNO_3 and HCl filter extraction methods and measurement of the dissolved Pb with ICP–MS. Tables 2, 4, and 6 show recoveries obtained with these SRM. The recoveries for all SRMs were ≥90 percent at the 95 percent confidence level.

TABLE 1—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/GLASS FIBER FILTER BLANKS SPIKED WITH LOW-LEVEL PB SOLUTION

	Ultrasonic extraction method	Hotblock extraction method
	$\mu g/m^3$*	$\mu g/m^3$*
n = 1	0.0000702	0.000533
n = 2	0.0000715	0.000482
n = 3	0.0000611	0.000509
n = 4	0.0000587	0.000427
n = 5	0.0000608	0.000449
n = 6	0.0000607	0.000539
n = 7	0.0000616	0.000481
Average	0.0000635	0.000489
Standard Deviation	0.0000051	0.000042
MDL**	0.0000161	0.000131

*Assumes 2000 m^3 of air sampled.
**MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

TABLE 2—RECOVERIES OF LEAD FROM NIST SRMS SPIKED ONTO GLASS FIBER FILTERS

Extraction method	Recovery, ICP–MS, (percent)			
	NIST 1547 plant	NIST 2709 soil	NIST 2583 dust	NIST 2582 paint
Ultrasonic Bath	100 ±4	98 ±1	103 ±8	101 ±0
Block Digestion	92 ±7	98 ±3	103 ±4	94 ±4

TABLE 3—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/QUARTZ FILTER BLANKS SPIKED WITH LOW-LEVEL PB SOLUTION

	Ultrasonic extraction method	Hotblock extraction method
	$\mu g/m^3$*	$\mu g/m^3$*
n = 1	0.000533	0.000274

TABLE 3—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/QUARTZ FILTER BLANKS SPIKED WITH LOW-LEVEL PB SOLUTION—Continued

	Ultrasonic extraction method	Hotblock extraction method
	μg/m³*	μg/m³*
n = 2	0.000552	0.000271
n = 3	0.000534	0.000281
n = 4	0.000684	0.000269
n = 5	0.000532	0.000278
n = 6	0.000532	0.000272
n = 7	0.000552	0.000261
Average	0.000560	0.000272
Standard Deviation	0.000055	0.000007
MDL**	0.000174	0.000021

*Assumes 2000 m³ of air sampled.
**MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

TABLE 4—RECOVERIES OF LEAD FROM NIST SRMS SPIKED ONTO QUARTZ FIBER FILTERS

Extraction method	Recovery, ICP–MS, (percent)			
	NIST 1547 plant	NIST 2709 soil	NIST 2583 dust	NIST 2582 paint
Ultrasonic Bath	101 ±6	95 ±1	91 ±5	93 ±1
Block Digestion	106 ±3	104 ±3	92 ±6	95 ±2

TABLE 5—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/PTFE FILTER BLANKS SPIKED WITH LOW-LEVEL PB SOLUTION

	Ultrasonic extraction method
	μg/m³*
n = 1	0.001775
n = 2	0.001812
n = 3	0.001773
n = 4	0.001792
n = 5	0.001712
n = 6	0.001767
n = 7	0.001778
Average	0.001773
Standard Deviation	0.000031
MDL**	0.000097

*Assumes 24 m³ of air sampled.
**MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

TABLE 6—RECOVERIES OF LEAD FROM NIST SRMS SPIKED ONTO PTFE FILTERS

Extraction method	Recovery, ICP–MS, (percent)			
	NIST 1547 plant	NIST 2709 soil	NIST 2583 dust	NIST 2582 paint
Ultrasonic Bath	104 ±5	93 ±1	108 ±11	96 ±3

15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. The sources of pollution generated with this procedure are waste acid extracts and Pb-containing solutions.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of

Government Relations and Science Policy, 1155 16th St. NW., Washington, DC 20036, *www.acs.org*.

16.0 Waste Management

16.1 Laboratory waste management practices must be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing all releases from hood and bench operations, complying with the letter and spirit of any sewer and discharge permits and regulations, and by complying with all solid and hazardous waste regulation. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society listed in Section 15.2 of this method.

16.2 Waste HNO_3, HCl, and solutions containing these reagents and/or Pb must be placed in labeled bottles and delivered to a commercial firm that specializes in removal of hazardous waste.

17.0 References

FACDQ (2007). Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs, submitted to the U.S. EPA December 2007. Available: *http://water.epa.gov/scitech/methods/cwa/det/upload/final-report-200712.pdf*.

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Appendix H to Part 50—Interpretation of the 1-Hour Primary and Secondary National Ambient Air Quality Standards for Ozone

1. General

This appendix explains how to determine when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm (235 $\mu g/m^3$) is equal to or less than 1. An expanded discussion of these procedures and associated examples are contained in the ''Guideline for Interpretation of Ozone Air Quality Standards.'' For purposes of clarity in the following discussion, it is convenient to use the term ''exceedance'' to describe a daily maximum hourly average ozone measurement that is greater than the level of the standard. Therefore, the phrase ''expected number of days with maximum hourly average ozone concentrations above the level of the standard'' may be simply stated as the ''expected number of exceedances.''

The basic principle in making this determination is relatively straightforward. Most of the complications that arise in determining the expected number of annual exceedances relate to accounting for incomplete sampling. In general, the average number of exceedances per calendar year must be less than or equal to 1. In its simplest form, the number of exceedances at a monitoring site would be recorded for each calendar year and then averaged over the past 3 calendar years to determine if this average is less than or equal to 1.

2. Interpretation of Expected Exceedances

The ozone standard states that the expected number of exceedances per year must be less than or equal to 1. The statistical term ''expected number'' is basically an arithmetic average. The following example explains what it would mean for an area to be in compliance with this type of standard. Suppose a monitoring station records a valid daily maximum hourly average ozone value for every day of the year during the past 3 years. At the end of each year, the number of days with maximum hourly concentrations above 0.12 ppm is determined and this number is averaged with the results of previous years. As long as this average remains ''less than or equal to 1,'' the area is in compliance.

3. Estimating the Number of Exceedances for a Year

In general, a valid daily maximum hourly average value may not be available for each day of the year, and it will be necessary to account for these missing values when estimating the number of exceedances for a particular calendar year. The purpose of these computations is to determine if the expected number of exceedances per year is less than or equal to 1. Thus, if a site has two or more observed exceedances each year, the standard is not met and it is not necessary to use the procedures of this section to account for incomplete sampling.

The term ''missing value'' is used here in the general sense to describe all days that do not have an associated ozone measurement.